

In addition, examples of the above novolak type epoxy resins include epoxy resins obtained by reaction of phenol novolak or cresol novolak with epichlorhydrin or methylepichlorhydrin.

Moreover, examples of the above unsaturated monobasic acid include acrylic acid, methacrylic acid, cinnamic acid, crotonic acid, sorbic acid, monomethylmalate, monopropylmalate, monobutylmalate, mono(2-ethylhexyl)malate, and the like.

Furthermore, these unsaturated monobasic acids may be used alone or in a combination of two or more types. The above reaction between epoxy resin and unsaturated monobasic acid is carried out using an esterification catalyst at a temperature preferably within the range of 60 to 140°C, and particularly preferably 80 to 120°C.

Known, commonly used compounds can be used as is for the above esterification catalyst, examples including various types of tertiary amines, such as triethylamine, N,N-dimethylbenzylamine, N,N-dimethylaniline, or diazabicyclooctane, and diethylamine hydrochlorides.

The number average molecular weight of the epoxy(meth)acrylate is preferably within the range of 450 to 2,500, and particularly preferably within the range of 500 to 2,200. In the case the molecular weight is less than 450, the resulting cured product becomes sticky and strength properties decrease. On the other hand, if the molecular weight exceeds 2,500, curing time becomes longer and productivity becomes inferior.

The above urethane(meth)acrylate is obtained by reacting polyol, polyisocyanate and hydroxyl group-containing (meth)acrylic compound. Examples of polyols used include polypropylene oxide, polyethylene oxide, polytetramethylene glycol, bisphenol A ethylene oxide addition product and bisphenol A propylene oxide addition product and other polyether polyols, polybutadienediol, polyisoprenediol, polyester ether polyols, polyester polyols, and the like.

Examples of the above polyisocyanate include 2,4-tolylenediisocyanate and its isomers or isomer compounds (abbreviated as TDI), diphenylmethane diisocyanate, hexamethylene diisocyanate, isophorone diisocyanate, xylene diisocyanate, hydrogenated xylene diisocyanate, dicyclohexylmethane diisocyanate, tolidine diisocyanate, naphthalene diisocyanate, triphenylmethane triisocyanate, Burnock D-750, Crisbon NX (manufactured by DAINIPPON INK AND CHEMICALS, INC.), Desmodule L (manufactured by Sumitomo-Bayer Co., Ltd.), Coronate L (manufactured by Nippon Polyurethane Co., Ltd.),

Takenate D102 (manufactured by Takeda Chemical Industries, Ltd.) and Isonate 143L (manufactured by Mitsubishi Chemical Corp.). These can be used alone or by combining two or more types. Among the above polyisocyanates, diisocyanates, and particularly TDI, is used preferably.

The hydroxyl group-containing (meth)acrylic compound is preferably a hydroxyl group-containing (meth)acrylic ester, examples of which include 2-hydroxyethyl(meth)acrylate, 2-hydroxypropyl(meth)acrylate and 3-hydroxybutyl(meth)acrylate; mono(meth)acrylates of alcohols having two hydroxyl groups such as polyethylene glycol mono(meth)acrylate and polypropylene glycol mono(meth)acrylate; addition products of  $\alpha$ -olefin epoxides and (meth)acrylic acid and addition products of carboxylic glycidyl esters and (meth)acrylic acid; and, partial (meth)acrylates of alcohols having three or more hydroxyl groups such as di(meth)acrylates of tris(hydroxyethyl)isocyanuric acid and pentaerythritol tri(meth)acrylate.

In addition, in producing the urethane(meth)acrylate of the present invention, a portion of the hydroxyl group-containing (meth)acrylic compound may be substituted with a compound such as a hydroxyl group-containing aryl ether or higher alcohol to an extent that does not impair the effect of the present invention.

Examples of hydroxyl group-containing aryl ether compounds include ethylene glycol monoaryl ether, diethylene glycol monoaryl ether, triethylene glycol monoaryl ether, polyethylene glycol monoaryl ether, propylene glycol monoaryl ether, dipropylene glycol monoaryl ether, tripropylene glycol monoaryl ether, polypropylene glycol monoaryl ether, 1,2-butylene glycol monoaryl ether, 1,3-butylene glycol monoaryl ether, hexylene glycol monoaryl ether, octylene glycol monoaryl ether, trimethylolpropane diaryl ether, glycerin diaryl ether, pentaerythritol triaryl ether and other aryl ether compounds of polyhydric alcohols, while aryl ethers having one hydroxyl group are preferable.

Examples of higher alcohols include decyl alcohol, undecyl alcohol, lauryl alcohol, tridecyl alcohol and stearyl alcohol.

As one example of a production method of the urethane(meth)acrylate of the present invention, polyether polyol and polyisocyanate are first reacted at  $\text{NCO}/\text{OH} = 2$  to 1.5 so that the number average molecular weight is preferably 500 to 30000 and particularly preferably 700 to 5000 to form a terminal isocyanate group-containing urethane pre-polymer, followed by reacting a hydroxyl group-containing acrylic compound with this

so that the hydroxyl groups are roughly equivalent to the isocyanate groups of said pre-polymer.

As an example of a different method, hydroxyl group-containing acrylic compound is first reacted with polyisocyanate followed by reacting the resulting isocyanate group-containing compound with polyether polyol to produce urethane(meth)acrylate preferably having a number average molecular weight of 500 to 30000, and more preferably 700 to 5000.

The polymerizable unsaturated monomer used in the curable resin composition of the present invention is that which is used in ordinary unsaturated polyester resin compositions, vinyl ester resins or vinyl urethane resin compositions within a range that does not impair the effect of the present invention, examples of which include styrene,  $\alpha$ -methylstyrene, chlorostyrene, dichlorostyrene, divinylbenzene, t-butylstyrene, vinyltoluene, vinyl acetate, diarylbutarate, triarylcyranurate, acrylic ester and methacrylic ester; methyl(meth)acrylate, ethyl(meth)acrylate, n-butyl(meth)acrylate, i-butyl(meth)acrylate, t-butyl(meth)acrylate, 2-ethylhexyl(meth)acrylate, lauryl(meth)acrylate, cyclohexyl(meth)acrylate, benzyl(meth)acrylate, stearyl(meth)acrylate, tridecyl(meth)acrylate, dicylopentenylxyethyl(meth) acrylate, ethylene glycol monomethylether(meth)acrylate, ethylene glycol monoethylether(meth)acrylate, ethylene glycol monobutylether(meth)acrylate, ethylene glycol monohexylether (meth)acrylate, ethylene glycol mono-2-ethylhexylether (meth)acrylate, diethylene glycol monomethylether(meth) acrylate, diethylene glycol monoethylether(meth)acrylate, diethylene glycol monobutylether(meth)acrylate, diethylene glycol monohexylether(meth)acrylate, diethylene glycol mono-2-ethylhexylether(meth)acrylate, dipropylene glycol monomethylether(meth)acrylate, dipropylene glycol monoethylether(meth)acrylate, dipropylene glycol monobutylether(meth)acrylate, dipropylene glycol monohexylether(meth)acrylate, dipropylene glycol mono-2-ethylhexylether(meth)acrylate, diethylene glycol di(meth)acrylate, dipropylene glycol di(meth)acrylate, neopentyl glycol di(meth)acrylate, 1,3-butylene glycol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, 2-hydroxy-1,3-dimethacryloxypropane, 2,2-bis[4-(methacryloxyethoxy)phenyl]propane, 2,2-bis[4-(methacryloxy-diethoxy)phenyl]propane, 2,2-bis[4-(methacryloxy-polyethoxy)phenyl]propane, tetraethylene glycol diacrylate,